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**(54) Method of Applying Rubber to a Substrate**

(57) The invention relates to the application of an unvulcanised rubber film to a substrate and is particularly applicable to the bonding of substrates using the rubber film as an adhesive. The method comprises causing relative frictional movement

between the unvulcanised rubber and the substrate to at least soften the contact surface of the unvulcanised rubber, and then moving the unvulcanised rubber and/or the substrate in relation to each other, whilst continuing said relative frictional movement, to leave a trail of the unvulcanised rubber on the surface.

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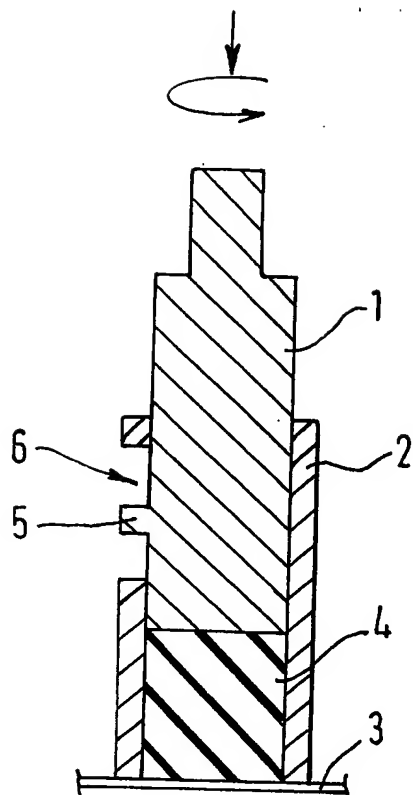


FIG. 1

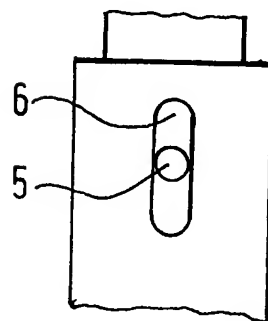


FIG. 2

## SPECIFICATION

## Method of Applying Rubber to a Substrate

This invention relates to the application of unvulcanised rubber films to substrates.

According to the present invention, a method of applying a film of an unvulcanised rubber to the surface of a substrate comprises causing relative frictional movement between the unvulcanised rubber and the substrate to at least soften the contact surface of the unvulcanised rubber, and then moving the unvulcanised rubber and/or the substrate in relation to each other, whilst continuing said relative frictional movement, to leave a trail of the unvulcanised rubber on the substrate. 5

By this method, films of unvulcanised rubbers may be applied e.g. as decoration, labelling, a potential adhesive, or to confer desired properties on the surface of the substrate e.g. compatibility with other materials or improvement in its ozone or general ageing resistance. In contrast to hot melt adhesion in which the energy is in the form of initial heat supplied to the adhesive which is rapidly dissipated, and in contrast to known hand-applied waxy permanent-tack adhesives in which the only energy supplied is the linear movement of the adhesive across a substrate, the method of the present invention involves a constant supply of energy which thus usually results in an improved bond strength and the ability to bond a wider range of substrates with a wider range of adhesives. 10 15

Examples of unvulcanised rubbers include thermoplastic rubbers (such as ABA block copolymers, e.g. styrene/butadiene which may be hydrogenated, polyurethanes and blends or grafts of polyethylene or polypropylene with EPDM or EP rubbers), and vulcanisable rubbers such as natural rubber, polychloroprene or SBR. Where the unvulcanised rubber is vulcanisable it may be vulcanised after being applied to the substrate if desired. Preferably the unvulcanised rubber has a molecular weight of more than 20,000 e.g. from 25,000 to  $10^7$ . The rubbery materials are further defined by having a tensile modulus at 300% elongation at 50°C of less than 7 MN/m<sup>2</sup>, preferably less than 4 MN/m<sup>2</sup> measured according to B.S. 903 part (ii). 20

Examples of suitable substrates include leather, synthetic leather (e.g. based on a polyurethane), wood, vulcanised rubber (foamed or unfoamed) and thermoplastic or thermoset plastics (foamed or unfoamed). Examples of suitable vulcanised rubbers include natural rubber, SBR, nitrile rubber and polyurethane rubber. If desired a vulcanised rubber composition which includes a high proportion of a resin (e.g. a hydrocarbon resin or a phenolic resin, such as t-butyl phenolic resin or terpene phenolic resin) may be used i.e. a so-called "resin rubber". Examples of suitable thermoplastic plastics include poly(vinyl chloride) and polyurethanes. The substrate may be reinforced, e.g. by textile such as nylon, and if the surface of the substrate is uneven it may be prebuffered. Examples of synthetic leathers are synthetic poromeric leathers (i.e. porous) available as Porvair or Corfam. Generally, suitable substrates include those materials used for making footwear e.g. an upper and/or a sole. 25 30

The unvulcanised rubber and/or substrate may be in a compound with conventional ingredients such as plasticisers, vulcanising agents, waxes, tackifiers, softeners, fillers, pigments, anti-oxidants and stabilisers. If desired a further rubber e.g. chlorinated natural rubber may be included in the unvulcanised rubber composition. The unvulcanised rubber, when in a composition with another ingredient or ingredients, is present in an amount of from 20 to 100% by weight, preferably from 30 to 100% by weight and advantageously from 40 to 100% by weight. Often an amount of from 70 to 100% is useful. The unvulcanised rubber is not a pressure sensitive adhesive i.e. one which in solvent-free form is permanently tacky. Such materials will adhere instantaneously to most substrates by the application of only very slight pressure. 35 40

If it is desired to vulcanise the unvulcanised rubber after application to each of two substrates, a carrier layer including vulcanising agents may be sandwiched between the two films and then heat and/or pressure applied as necessary. 45

The unvulcanised rubber may be in the form of a rod held in the chuck of a rotating or oscillating drill. When the surface of the rod in contact with the substrate has softened which will generally be above 50°C and may be above 100°C in practice, the rod is moved across the surface of the substrate so that a trail of the rubber is deposited. If the unvulcanised rubber is a relatively soft, pliable material it may be contained in an inert sleeve under suitable pressure (mechanical or otherwise) so that it is continuously forced out of the end of the sleeve onto the substrate. 50

One such arrangement will now be described by way of example only with reference to the accompanying drawings in which:

Figure 1 is a cross-sectional view of a device for trailing low modulus (soft, pliable) unvulcanised rubbers, and 55

Figure 2 is a side view of the drive pin and slot of Figure 1.

In Figure 1, a piston 1 slidably fits partially within a cylinder 2 to define a cavity 4 into which an unvulcanised rubber can be inserted. The surface of the rubber is contacted with that of the substrate 3. The piston 1 is rotatable by means of a motor (not shown) and the cylinder 2 is rotatable by means of the piston 1 transmitting its rotation to the cylinder 2 through a slidable pin 5/slot 6 assembly. In use, the piston 1 is rotated by a motor and causes the cylinder 2 also to rotate. The pressure and rotational motion of the piston is thus imparted to the rubber causing it to soften on the substrate 60

surface. The device can then be moved along a predetermined path so as to trail the rubber upon the substrate whilst still rotating the rubber.

The relative movement between the rubber and the substrate may be produced in any convenient manner. One or both components may be moved. The friction may be achieved by rotatory, angular or linear movement and may be continuous (i.e. in one direction) or oscillatory. An alternative to mechanical movement is the use of an ultrasonic frequency welding technique which creates rapid small vibratory movements between the surfaces.

The conditions of the relative frictional movement, such as speed and duration of the movement and pressure between the rubber and the substrate, are such as to at least soften the friction surface of the rubber and will depend upon the materials used. External heating is not usually necessary but may be employed if desired. Examples of suitable continuous relative rotary movement speeds are from 750 to 20,000 revolutions per minute. When an oscillatory movement is employed, this may be performed over a few degrees of arc or, in the case of linear movement, over about 0.1 to 6 mm, preferably 1 to 4 mm, and at a frequency of 50 to 200 Hz, especially 100 Hz.

A typical rate of frictional movement is between 2.5 and 10 m sec<sup>-1</sup> and a pressure of usually only about 335 to 1340 gcm<sup>-2</sup> (5 to 20 p.s.i.) is required. By comparison, prior known waxy hand-applied permanent-tack stick adhesives require a tip pressure in the order of 1340 to 6700 gcm<sup>-2</sup> (20 to 100 p.s.i.) at a movement of about 0.1 to 0.5 m sec<sup>-1</sup>. Another contrasting factor is that by using the method of the present invention not only is the temperature of the unvulcanised rubber raised but so is that of the substrate and this facilitates the wetting action of the unvulcanised rubber thus improving the resultant bond strength. It has been found that, possibly for that very reason, it is often unnecessary to treat the surface of a substrate prior to bonding even in the case of substrates which normally would have to be pretreated in order to be bonded to particular unvulcanised rubbers applied by a different method e.g. in solution.

Even if the contact surface of the unvulcanised rubber is heated by the friction to a semi-liquid state, because of the small proportion of material that is in this state it can be cooled very rapidly and therefore degradation of it or the substrate is unlikely.

If it is desired to reactivate the trail of the unvulcanised rubber, e.g. to use it as an adhesive to bond the substrate to another substrate, this may be done by using a suitable solvent or by heating the trail to soften it e.g. with infra-red, ultrasonic, radio frequency or induction heating methods or by a friction welding technique.

The rubber and/or the substrate may be frozen to harden it for the relative movement.

Separate films may be applied simultaneously by suitable equipment. Shaped films may be applied e.g. as a shoe outline by using e.g. linear or angular friction techniques.

The substrate may be pre-treated i.e. treated before it is moved in relation to an unvulcanised rubber to enhance its adherability to the rubber film, for example the substrate may be pre-buffed or pre-treated with a chemical treatment agent e.g. aldehyde condensation resin-forming ingredients such as resorcinol and hexamethylene tetramine, acidified sodium hypochlorite, concentrated nitric acid, a chloroisocyanuric acid such as trichloroisocyanuric acid suitably as a solution e.g. in ethyl acetate or as a powder, an alkali metal salt of a chloroisocyanuric acid e.g. sodium dichloroisocyanurate, (such salts are commercially available under the trade name 'Fi-clor'), UV irradiation, glow discharge or flame-treatment. The term 'aldehyde condensation resin-forming ingredients' as used in this specification includes a partially condensed aldehyde resin. Alternatively and preferably a chemical treatment agent can be applied 'in situ' as the rubber film is applied to the substrate. This can be done either by forming or drilling at least one cavity in the rubber body and packing the cavity or cavities with a treatment agent or by forming into the required shape e.g. by moulding a blend of an unvulcanised rubber and a treatment agent such as one of those already mentioned.

If desired the treatment agent may be supported in an inert medium e.g. a wax. When the rubber is in the form of a rod the cavity or cavities preferably extend longitudinally of the rod.

Incompatible substrates may be bonded by applying a rubber film to each of them by the method of the present invention and then bonding the films e.g. by softening at least one of them and allowing the film or films to solidify in contact. Alternatively, a rubber interlayer may be placed between the film coated substrates and then the interlayer and usually also the films are softened and the assembly is allowed to cool.

The method of the present invention may be used in the manufacture of footwear. Generally, a footwear upper is of leather, synthetic leather, vulcanised rubber or thermoplastic plastics. The upper has to be attached to the sole of the article of footwear and previously this has usually been done using a proprietary adhesive. If the adhesive is based on a conventional rubber solution e.g. one based on polychloroprene, this usually must be coated onto the sole and upper and allowed to dry to a slightly tacky state before the two components are pressed together. If a polyurethane-based adhesive is used, this must usually be coated onto both components and dried completely before bonding. The adhesive layer on the sole is then softened, e.g. using an infra red lamp, and the two components are pressed together. Both these methods are time-consuming because adhesive must be applied to sole and upper individually and the solvent in the adhesive allowed to evaporate before contacting the sole and upper.

In addition it is usual to buff the adhering surfaces of the sole and upper before applying an adhesive.

- It is proposed to have an upper comprising leather, synthetic leather, vulcanised rubber, thermoset or thermoplastic plastics having a layer or layers of an unvulcanised rubber bonded to it by the method of the present invention at places where the upper will eventually be attached to a sole. In order to attach the upper to a sole it is usually only necessary to soften at least the surface of the rubber, e.g. by infra red, ultrasonic, radio frequency or induction heating methods, and press the softened surface against the sole which preferably also has had a trail of unvulcanised rubber applied to it. Alternatively the surface of the rubber may be softened by using a friction welding tool. On cooling, a bond is obtained between the upper and the sole. No messy solvents are involved, and the process of bonding the upper to the sole is quicker and easier as it is not usually necessary to apply a trail of unvulcanised rubber to both upper and sole. Another advantage is that an upper can be easily transported already having a potential adhesive layer which can be bonded to a sole when required. Examples of other applications of the method of the present invention are in the fabrication of harnessing, furniture, handbags, flexible or rigid containers and boats.
- The method of the present invention is illustrated by the following Examples in which IB and IIB are for comparison only.

#### Example I

Leather was bonded to itself by two methods:

- IA) By rotating at a speed of 3000 revolutions/minute and a pressure of about 1340 g/cm<sup>2</sup> (20 p.s.i.) an unvulcanised rubber on each surface to be bonded, and trailing the rubber along each surface whilst maintaining the rotational motion, reactivating the trails by infra red heating to a surface temperature of 80°C and then assembling them in an air press for 10 seconds. After cooling for 1 hour the adhesion of the sample was peel tested on an Instron machine.
- IB) By applying to each surface to be bonded a solution of an unvulcanised rubber in methylethyl ketone and allowing the adhesive to dry for 24 hours. The adhesive coats were then reactivated by infra red heating to a surface temperature of 80°C and then placed face to face in an air press for 10 seconds. After cooling for 1 hour the adhesion of the sample was peel tested on an Instron machine.

|    |   | <b>Results</b>   |  |
|----|---|--|--|
|    |   | <i>Peel strength for method 1A in lb/inch for a 1" strip</i> | <i>Peel strength for method IB in lb/inch for a 1" strip</i> |
| 30 | <i>Unvulcanised Rubber</i>  |  |  |
|    | Polyurethane (a polyester-based urethane available as Desmocoll 400)  | 30.8   | 12.6   |
| 35 | Polyurethane (a polyester-based urethane available as Desmocoll 530T) | 50.6   | 13.3   |
| 40 | Polyurethane (a polyester-based urethane available as Estane 5713)    | 36.1   | 14.8   |

- Thus a substantially improved bond is obtained by using the method of the present invention compared to known "solution" techniques.

#### Example II

Leather was bonded by two methods to the polished untreated surface of a "resin rubber" often used to make shoe soles (a styrene/butadiene based composition).

- IIA) By rotating at a speed of 3000 revolutions/minute and a pressure of about 1340 g/cm<sup>2</sup> (20 p.s.i.) an unvulcanised rubber on each substrate and trailing the rubber along each surface whilst maintaining the rotational motion, reactivating the trails by infra red heating to a surface temperature of 80°C and then assembling them in an air press for 10 seconds. After cooling for 1 hour the adhesion of the sample was peel tested on an Instron machine.
- IIB) By applying to each substrate a solution of an unvulcanised rubber in methyl ethyl ketone and allowing the adhesive to dry for 24 hours. The adhesive coats were then reactivated by infra red heating to a surface temperature of 80°C and then placed face to face in an air press for 10 seconds. After cooling for 1 hour the adhesion of the sample was peel tested on an Instron machine.

|    |  | Result  |   |
|----|--|---|---|
|    |  | Peel strength for<br>method IIA in lb/<br>inch for a 1" strip | Peel strength for<br>method IIB in lb/<br>inch for a 1" strip |
|    | Unvulcanised Rubber  |   |   |
| 5  | Polyurethane<br>(Desmocoll 400T)   | 20  | 2   |
|    | This result is significant because it illustrates that with the method of the present invention prebuffing of the substrate is not essential whereas using known solution techniques there is a negligible bond for certain substrates in the absence of prebuffing.   |   |   |
|    | <b>Example III</b>   |   |   |
| 10 | A prebuffed "resin rubber" (vulcanised**) often used to make shoe soles was bonded to itself by:<br>i) rotating at a speed of 3000 revolutions/minute and a pressure of about 1340 g/cm <sup>2</sup> (20 p.s.i.) an unvulcanised rubber composition* onto each of two resin rubber strips and trailing the rubber onto the strips. |   |   |
| 15 | ii) reactivating the trails by infra red heating to a surface temperature of 80°C and then assembling them in an air press for 10 seconds.   |   |   |
|    | iii) After cooling for 1 hour the adhesion of the sample was peel tested on an Instran machine. The peel strength was 20 lb/inch for a 1" strip.   |   |   |
|    | * The rubber composition comprised 175 parts of a zinc resinate (available as Crayvallac 570) and 100 parts of natural rubber smoked sheet.  |   |   |
| 20 | ** A styrene/butadiene copolymer.  |   |   |
|    | <b>Example IV</b>  |   |   |
|    | Example III was repeated with the following rubber composition substituted for the natural rubber: 130 parts of a terpene phenolic resinate (available as Crayvallac 570 from Cray Valley Products) and 100 parts of equal amounts of two styrene/butadiene block copolymers available as  |   |   |
| 25 | Cariflex TR 1101 and TR 1102.  |   |   |
|    | The resulting peel strength for a 1" strip was 40 lb/inch.   |   |   |
|    | <b>Claims</b>  |   |   |
|    | 1. A method of applying a film of an unvulcanised rubber to the surface of a substrate comprises causing relative frictional movement between the unvulcanised rubber and the substrate to at least  |   |   |
| 30 | soften the contact surface of the unvulcanised rubber and then moving the unvulcanised rubber and/or the substrate in relation to each other, whilst continuing said frictional movement to leave a trail of the unvulcanised rubber on the substrate.   |   |   |
|    | 2. A method according to claim 1, wherein the rubber is a vulcanisable composition.  |   |   |
|    | 3. A method according to claim 1, wherein the rubber is thermoplastic.   |   |   |
| 35 | 4. A method according to claim 1, 2 or 3, wherein the rubber is a polyurethane.  |   |   |
|    | 5. A method according to any preceding claim, wherein the rubber has a molecular weight of more than 20,000.   |   |   |
|    | 6. A method according to any preceding claim, wherein the rubber has a molecular weight of from 25,000 to 10 <sup>7</sup> .  |   |   |
| 40 | 7. A method according to any preceding claim, wherein the rubber is present in a composition in an amount of from 30 to 100% by weight.  |   |   |
|    | 8. A method according to any preceding claim, wherein the rubber is present in a composition in an amount of from 40 to 100% by weight.  |   |   |
|    | 9. A method according to any preceding claim, wherein the rubber is present in a composition in  |   |   |
| 45 | an amount of from 70 to 100% by weight.  |   |   |
|    | 10. A method according to any preceding claim, wherein the surface of the substrate softens above 50°C.  |   |   |
|    | 11. A method according to any preceding claim, wherein the surface of the substrate softens above 100°C.   |   |   |
| 50 | 12. A method according to any preceding claim, wherein the unvulcanised rubber has a tensile modulus at 300% elongation at 50°C of less than 4 MN/m <sup>2</sup> .   |   |   |
|    | 13. A method according to any preceding claim, wherein the relative frictional movement is rotatory, angular or linear.  |   |   |
|    | 14. A method according to any preceding claim, wherein the relative frictional movement is   |   |   |
| 55 | between 2.5 and 10 m/sec.  |   |   |
|    | 15. A method according to any of claims 1 to 14, wherein the relative frictional movement is rotatory from 750 to 20,000 revolutions per minute.   |   |   |
|    | 16. A method according to any of claims 1 to 14, wherein the relative frictional movement is oscillatory at a frequency of 50 to 200 Hz.   |   |   |
| 60 | 17. A method according to claim 16, wherein the oscillatory movement is linear over 0.1 to 6 mm.   |   |   |

18. A method according to claim 17, wherein the oscillatory movement is linear over 1 to 4 mm.
19. A method according to any preceding claim, wherein the substrate is substantially stationary, and the unvulcanised rubber is moved.
20. A method according to any preceding claim, wherein the unvulcanised rubber is contained in  
5 an inert sleeve. 5
21. A method according to any preceding claim, wherein the substrate is a footwear component.
22. A method of applying a film of an unvulcanised rubber to the surface of a substrate substantially as herein described with reference to Figure 1 or 2.
23. A method of applying a film of an unvulcanised rubber to the surface of a substrate  
10 substantially as described in any one of the Examples. 10
24. A method of applying a film of an unvulcanised rubber to the surface of a substrate according to claim 1 and substantially as herein described.
25. A substrate having a trail of unvulcanised rubber when made by the method according to any preceding claim.
- 15 26. A method of bonding a substrate to a second substrate of the same or different material 15 comprises applying to each substrate an unvulcanised rubber trail according to any one of claims 1 to 24, reactivating the trails and solidifying them in contact.